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(71) Applicant (*for all designated States except US*): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): HAFNER, Andreas [CH/CH]; Bendenweg 3, CH-3177 Laupen (CH). VAN DER SCHAAF, Paul, Adriaan [NL/CH]; Impasse du Castel 9, CH-1700 Fribourg (CH). MÜHLEBACH, Andreas [CH/CH]; Les Grands Esserts 7, CH-1782 Belfaux (CH).

(74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).

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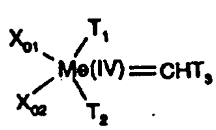
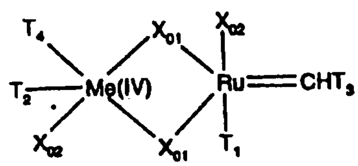

(I)


(Ia)

(57) Abstract

A solventless polymerisable composition comprising (a) at least one strained cycloolefin that is liquid or is meltable without decomposition, and (b) a catalytic amount of at least one compound of formula (I) or (Ia) or a mixture of compounds of formulae (I) and (Ia), wherein Me is ruthenium or osmium; T_1 and T_2 are each independently of the other a tertiary phosphine or T_1 and T_2 together form a ditertiary diphosphine; T_3 is hydrogen, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having from one to three hetero atoms selected from the group -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, -NO_2 or by halogen; T_4 is C_6-C_{16}arene or C_4-C_{15}heteroarene each of which is unsubstituted or substituted by from one to three C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br substituents, and X_{01} and X_{02} are each independently of the other halogen. The compositions are suitable for the production of mouldings and coatings.

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Polymerisable composition and polymerisation method

The present invention relates to a solventless polymerisable composition comprising a strained cycloolefin and a ruthenium(IV) or osmium(IV) carbene, to a method of polymerising the composition, and to the use of the composition in the production of mouldings.

The thermal metathesis polymerisation of strained cycloolefins has recently been gaining increasing importance. The polymerisation requires the use of catalysts. Known catalysts are mainly transition metal compounds. While, as a rule, systems consisting of a catalyst and co-catalyst have been used in the first instance (see, for example, US 4 060 468 and WO 93/13171), one-component catalysts are also known [Thoi, H.H., Ivin, K.J., Rooney, J.J., J. Mol. Catal. 15:245-270 (1982)]. WO 93/20111 discloses ruthenium(IV) and osmium(IV) compounds having a $=CH-CH=CR_1R_2$ group bonded to the metal atoms as catalysts for thermal metathesis polymerisation. Those "metal carbenes" are sparingly soluble compounds, so that polymerisation is possible only in polar and, where appropriate, protic solutions. The same catalysts are described by Kanaoka and Grubbs [Kanaoka, S., Grubbs, R.H., Macromolecules 28:4707-4713 (1995)] under the same conditions of solution polymerisation for the preparation of copolymers with silicon-containing norbornene derivatives. In that procedure the polymers have to be isolated and purified and also converted into a processible form, for example granules. For the production of shaped articles it is then necessary to employ in addition thermoplastic shaping procedures. The large number of processing steps generally results in a reduction in the mechanical and other performance properties, for example in discoloration. The use of solvents and the additional process steps are so disadvantageous from ecological and economic standpoints that industrial application is out of the question. In addition, the direct processing of solvent-containing systems to form bubble-free and homogeneous mouldings is either not possible at all or is possible only with difficulty, but such processing is necessary, however, because on the one hand the solvents used adversely affect the mechanical properties (for example there may be a plasticiser effect) and those properties will change until all the solvent has been lost, and on the other hand a constant release of solvent is ecologically harmful.

Fraser et al. [Fraser, C., Hillmyer, M., Gutierrez, E., Grubbs, R.H., Polym. Prepr. 36:237-238 (1995)] disclose for the first time $[(C_6H_{11})_3P]_3(C_6H_5-CH=)RuCl_2$ (a ruthenium carbene) as

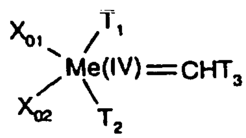
thermal catalyst for the polymerisation of mixtures of cyclooctadiene and 4,7-dihydro-1,3-oxepine. That ruthenium carbene is a very active catalyst which is capable of initiating polymerisation even at room temperature. Here too, polar and halogenated solvents, specifically a concentrated solution of the catalyst in methylene chloride, are used in the polymerisation, so that the above-described disadvantages are not overcome.

The preparation of $[(C_6H_{11})_3P]_3(C_6H_5\text{-}CH\text{=})RuCl_2$ and other ruthenium carbene compounds is disclosed by Schwab et al. [Schwab, P., France, M.B., Ziller, J.W., Grubbs, R.H., Angew. Chem. 107:2179-2181 (1995)]. They are described as highly active catalysts for ring-opening metathesis polymerisation. For polymerisations carried out with norbornene and substituted cyclobutenes, either methylene chloride or benzene is used as solvent.

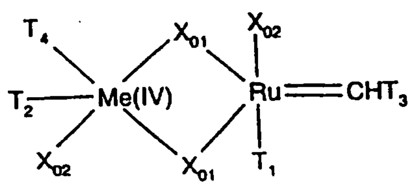
It should also be mentioned that Tanielian et al. [Tanielian, C., Kiennemann, A., Osparpucu, T., Can. J. Chem. 57:2022-2027 (1979)] describe that the ruthenium compound $RuCl_2[P(C_6H_5)_3]_3$ is deactivated by dicyclopentadiene and no polymers are formed by metathesis polymerisation.

It has now surprisingly been found that those ruthenium carbenes have excellent solubility in monomeric strained cycloolefins even when the monomers do not contain polar groups or substituents and are composed only of carbon and hydrogen. This allows bulk polymerisation and the direct production of mouldings. Despite the high activity of the catalysts, dilution and reduction of the reactivity with a polar solvent is unnecessary, and it is possible to prepare directly-processible compositions from the catalyst-containing monomer. The disadvantages resulting from a solvent content, such as the risk of bubble formation and a change in the mechanical properties, no longer exist.

The invention relates firstly to a solventless polymerisable composition comprising
(a) at least one strained cycloolefin that is liquid or is meltable without decomposition, and
(b) a catalytic amount of at least one compound of formula I or Ia or a mixture of compounds of formulae I and Ia



(I),



(Ia),

wherein

Me is ruthenium or osmium;

T_1 and T_2 are each independently of the other a tertiary phosphine or T_1 and T_2 together form a ditertiary diphosphine;

T_3 is hydrogen, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having from one to three hetero atoms selected from the group -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or by halogen;

T_4 is C_6-C_{16}arene or C_4-C_{15}heteroarene each of which is unsubstituted or substituted by from one to three C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br substituents, and

X_{01} and X_{02} are each independently of the other halogen.

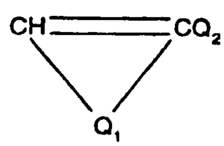
Within the scope of this invention, a solventless composition contains from 0 to 4 %, preferably from 0 to 2 %, solvent, based on the cycloolefin.

The cyclic olefins may be monocyclic or polycyclic condensed and/or bridged and/or linked ring systems, for example having from two to four rings, which are unsubstituted or substituted and may contain hetero atoms, for example an O, S, N or Si atom, in one or more rings and/or may contain condensed aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual cyclic rings may contain from 3 to 16, preferably from 3 to 12 and especially from 3 to 8, ring members.

The cyclic olefins may contain further non-aromatic double bonds, preferably, depending upon the ring size, from 2 to 4 such additional double bonds. The ring substituents are inert, that is to say they do not adversely affect the chemical stability and the thermal stability of the ruthenium and osmium catalysts. The cycloolefins are strained rings or ring systems. Individual rings and ring systems having from 5 to 8 carbon atoms in the ring are especially preferred.

When the cyclic olefins contain more than one double bond, for example from 2 to 4 double bonds, or when mixtures of strained cycloolefins having one double bond and strained cycloolefins having at least two double bonds, for example from 2 to 4 double bonds, are used, then, depending upon the reaction conditions, the monomer chosen and the amount of catalyst, it is also possible for cross-linked polymerisates to be formed.

In a preferred embodiment of the composition according to the invention, the cycloolefins correspond to formula II



(II),

wherein

Q_1 is a radical having at least one carbon atom which, together with the $-CH=CQ_2-$ group, forms an at least 3-membered alicyclic ring which may contain one or more hetero atoms selected from the group Si, P, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, $-NO_2$, $R_1R_2R_3Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}hydroxyalkyl, C_1-C_{20}haloalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms, when present, are substituted by -CO-O-CO- or by $-CO-NR_5-CO-$; or wherein an alicyclic, aromatic or heteroaromatic ring has been fused to adjacent carbon atoms of the alicyclic ring, the former ring being unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_1-C_6cyanoalkyl, C_3-C_8-

cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{15}heteroaryl, C_4-C_{16}-heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO-, -SO_2-, -O-C(O)-, -C(O)-O-, -C(O)-NR_5-, -NR_{10}-C(O)-, -SO_2-O- or -O-SO_2-; R_1, R_2 and R_3 are each independently of the others C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; R_4 and R_{13} are each independently of the other C_1-C_{20}alkyl, C_1-C_{20}-haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_{12}alkoxy or by C_3-C_8cycloalkyl; R_6, R_7 and R_8 are each independently of the others C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; and u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{12}alkoxy, halogen, -CN or R_{11}-X_2- wherein R_{11} is C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl and X_2 is -C(O)-O- or -C(O)-NR_{12}- wherein R_{12} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

the above-mentioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, -NO_2, -CN or by halogen, and the hetero atoms of the afore-mentioned heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group -O-, -S-, -NR_9- and -N=; and R_9 is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl.

Fused-on alicyclic rings contain preferably from 3 to 8, especially from 5 to 8 and more especially 5 or 6, ring carbon atoms.

When an asymmetric centre is present in the compounds of formula I, the compounds may occur in optically isomeric forms. Some compounds of formula I may occur in tautomeric forms (for example keto-enol tautomerism). When an aliphatic C=C double bond is present, geometric isomerism (E-form or Z-form) may occur. Exo-endo configurations are also possible. The formula I therefore includes all possible stereoisomers present in the form of enantiomers, tautomers, diastereoisomers, E/Z-isomers or mixtures thereof.

In the definitions of the substituents, the alkyl, alkenyl and alkynyl groups may be straight-chain or branched. The same applies also to the (or each) alkyl moiety of alkoxy, alkylthio

and alkoxycarbonyl and other alkyl-containing groups. Those alkyl groups contain preferably from 1 to 12, especially from 1 to 8 and more especially from 1 to 4, carbon atoms. Those alkenyl and alkynyl groups contain preferably from 2 to 12, especially from 2 to 8 and more especially from 2 to 4, carbon atoms.

Alkyl includes, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Hydroxyalkyl includes, for example, hydroxymethyl, hydroxyethyl, 1-hydroxyisopropyl, 1-hydroxy-n-propyl, 2-hydroxy-n-butyl, 1-hydroxyisobutyl, 1-hydroxy-sec-butyl, 1-hydroxy-tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Haloalkyl includes, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl and also halogenated, especially fluorinated or chlorinated, alkanes, for example isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Alkenyl includes, for example, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Cycloalkyl is preferably C_5-C_8cycloalkyl, especially C_5- or C_6-cycloalkyl. Some examples are cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cyanoalkyl includes, for example, cyanomethyl (methylnitrile), cyanoethyl (ethylnitrile), 1-cyanoisopropyl, 1-cyano-n-propyl, 2-cyano-n-butyl, 1-cyano-isobutyl, 1-cyano-sec-butyl, 1-cyano-tert-butyl and the various isomeric cyanopentyl and cyanohexyl radicals.

Aralkyl contains preferably from 7 to 12 carbon atoms and especially from 7 to 10 carbon atoms. It may be, for example, benzyl, phenethyl, 3-phenylpropyl, α-methylbenzyl, phenbutyl or α,α-dimethylbenzyl.

Aryl preferably contains from 6 to 10 carbon atoms. It may be, for example, phenyl, pentaline, indene, naphthalene, azulene or anthracene.

Heteroaryl preferably contains 4 or 5 carbon atoms and one or two hetero atoms from the group O, S and N. It may be, for example, pyrrole, furan, thiophene, oxazole, thiazole, pyridine, pyrazine, pyrimidine, pyridazine, indole, purine or quinoline.

Heterocycloalkyl preferably contains 4 or 5 carbon atoms and one or two hetero atoms from the group O, S and N. It may be, for example, oxirane, azirine, 1,2-oxathiolane, pyrazoline, pyrrolidine, piperidine, piperazine, morpholine, tetrahydrofuran or tetrahydrothiophene.

Alkoxy is, for example, methoxy, ethoxy, propyloxy, isopropyloxy, n-butyloxy, isobutyloxy and tert-butyloxy.

Within the scope of this invention, an alkali metal is to be understood as being lithium, sodium, potassium, rubidium or caesium, especially lithium, sodium or potassium.

Within the scope of this invention, an alkaline earth metal is to be understood as being beryllium, magnesium, calcium, strontium or barium, especially magnesium or calcium.

In the above definitions, halogen is to be understood as being fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Compounds of formula II that are especially suitable for the composition according to the invention are those wherein Q_2 is hydrogen.

Also preferred for the composition are compounds of formula II in which the alicyclic ring formed by Q_1 together with the $-CH=CQ_2-$ group has from 3 to 16, preferably from 3 to 12,

especially from 3 to 8, and more especially from 5 to 8, ring atoms, and which may be monocyclic, bicyclic, tricyclic or tetracyclic ring systems.

It is especially advantageous when the composition according to the invention comprises compounds of formula II wherein

Q_1 is a radical having at least one carbon atom which, together with the -CH=CQ$_2$- group, forms a 3- to 20-membered alicyclic ring which may contain one or more hetero atoms selected from the group Si, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, -NO$_2$, $R_1R_2R_3Si$-(O)$_u$-, -COOM, -SO$_3$M, -PO$_3$M, -COO(M$_1$)$_{1/2}$, -SO$_3$(M$_1$)$_{1/2}$, -PO$_3$(M$_1$)$_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4-cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}-heteroaryl, C_4-C_{12}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms in that radical Q_1 are substituted by -CO-O-CO- or by -CO-NR$_5$-CO-; or wherein an alicyclic, aromatic or heteroaromatic ring may have been fused to adjacent carbon atoms, which ring is unsubstituted or substituted by halogen, -CN, -NO$_2$, $R_6R_7R_8Si$-, -COOM, -SO$_3$M, -PO$_3$M, -COO(M$_1$)$_{1/2}$, -SO$_3$(M$_1$)$_{1/2}$, -PO$_3$(M$_1$)$_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}-aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}heteroaryl, C_4-C_{12}heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO-, -SO$_2$-, -O-C(O)-, -C(O)-O-, -C(O)-NR$_5$-, -NR$_{10}$-C(O)-, -SO$_2$-O- or -O-SO$_2$-; and R_1, R_2 and R_3 are each independently of the others C_1-C_6alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_6alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_6-alkoxy or by C_3-C_6cycloalkyl; R_6, R_7 and R_8 are each independently of the other C_1-C_6-alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_6alkoxy, halogen, -CN or R_{11}-X_2- wherein R_{11} is C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl and X_2 is -C(O)-O- or -C(O)-NR$_{12}$- wherein R_{12} is hydrogen, C_1-C_6alkyl, phenyl or benzyl;

and the cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, -NO$_2$, -CN or by halogen, and the

hetero atoms of the heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group -O-, -S-, $-NR_9-$ and -N=; and R_9 is hydrogen, C_1-C_6alkyl, phenyl or benzyl.

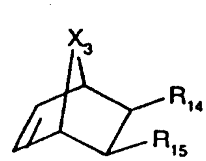
From that group preference is given to those compounds of formula II wherein

Q_1 is a radical having at least one carbon atom which, together with the $-CH=CQ_2-$ group, forms a 3- to 10-membered alicyclic ring which may contain a hetero atom selected from the group Si, O, N and S, and which is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_1R_2R_3Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or by R_4-X-; or wherein an alicyclic, aromatic or heteroaromatic ring may have been fused to adjacent carbon atoms, which ring is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or by R_{13}-X_1-; R_1, R_2 and R_3 are each independently of the others C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} are each independently of the other C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl or C_3-C_6cycloalkyl; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO- or $-SO_2-$; R_6, R_7 and R_8 are each independently of the others C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; and

Q_2 is hydrogen.

The composition according to the invention comprises especially norbornene and norbornene derivatives, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene or cyclododecene. Surprisingly it has been found that in the case of substituted norbornene the polymerisation also proceeds well when the substituents are in the endo-position.

Of the norbornene derivatives, special preference is given to those corresponding to formula III



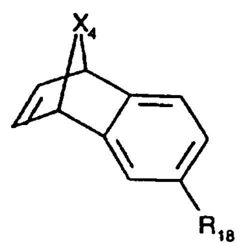
(III),

wherein

X_3 is $-CHR_{16}-$, oxygen or sulfur;

R_{14} and R_{15} are each independently of the other hydrogen, -CN, trifluoromethyl, $(CH_3)_3Si-O-$, $(CH_3)_3Si-$ or $-COOR_{17}$; and

R_{16} and R_{17} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; or to formula IV



(IV),

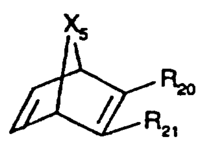
wherein

X_4 is $-CHR_{19}-$, oxygen or sulfur;

R_{18} is hydrogen, C_1-C_6alkyl or halogen; and

R_{19} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula V



(V),

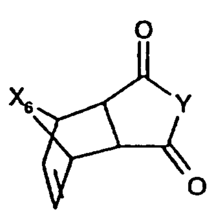
wherein

X_5 is $-CHR_{22}-$, oxygen or sulfur;

R_{20} and R_{21} are each independently of the other hydrogen, CN, trifluoromethyl, $(CH_3)_3Si-O-$, $(CH_3)_3Si-$ or $-COOR_{23}$; and

R_{22} and R_{23} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula VI,



(VI),

wherein

X_6 is $-CHR_{24}-$, oxygen or sulfur;

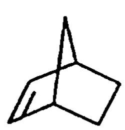
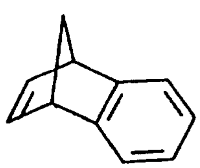
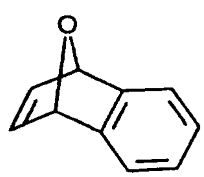
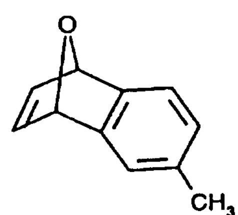
Y is oxygen or $>N-R_{25}$,

R_{24} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; and
R_{25} is hydrogen, methyl, ethyl or phenyl.

It has surprisingly been found that using the Ru and Os catalysts to be used according to the invention it is possible to polymerise even dicyclopentadiene, oligopentadienes and Diels-Alder adducts of cyclopentadiene with cycloolefins or open-chain dienes. Those monomers are a preferred sub-group of strained cycloolefins, because their polymerisation was not to be expected.

Another preferred sub-group of monomers is formed by those composed only of carbon and hydrogen.

The following compounds of formula I which may be preparable by Diels-Alder reactions are some specific examples, it being possible for the oxanorbornene derivatives also to be norbornene derivatives and *vice versa*:

 ,  ,  , 

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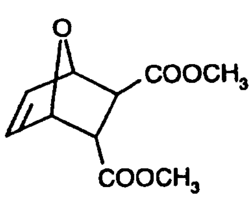
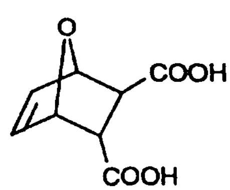
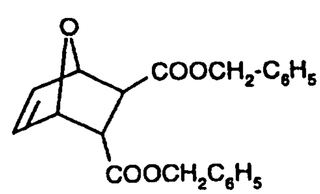


, 

, 

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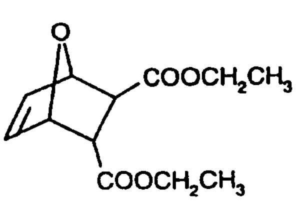
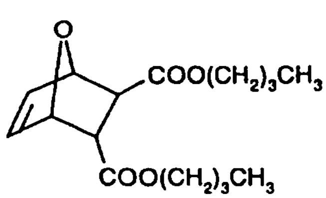
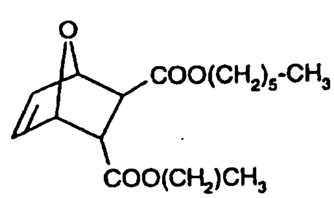


, 

, 

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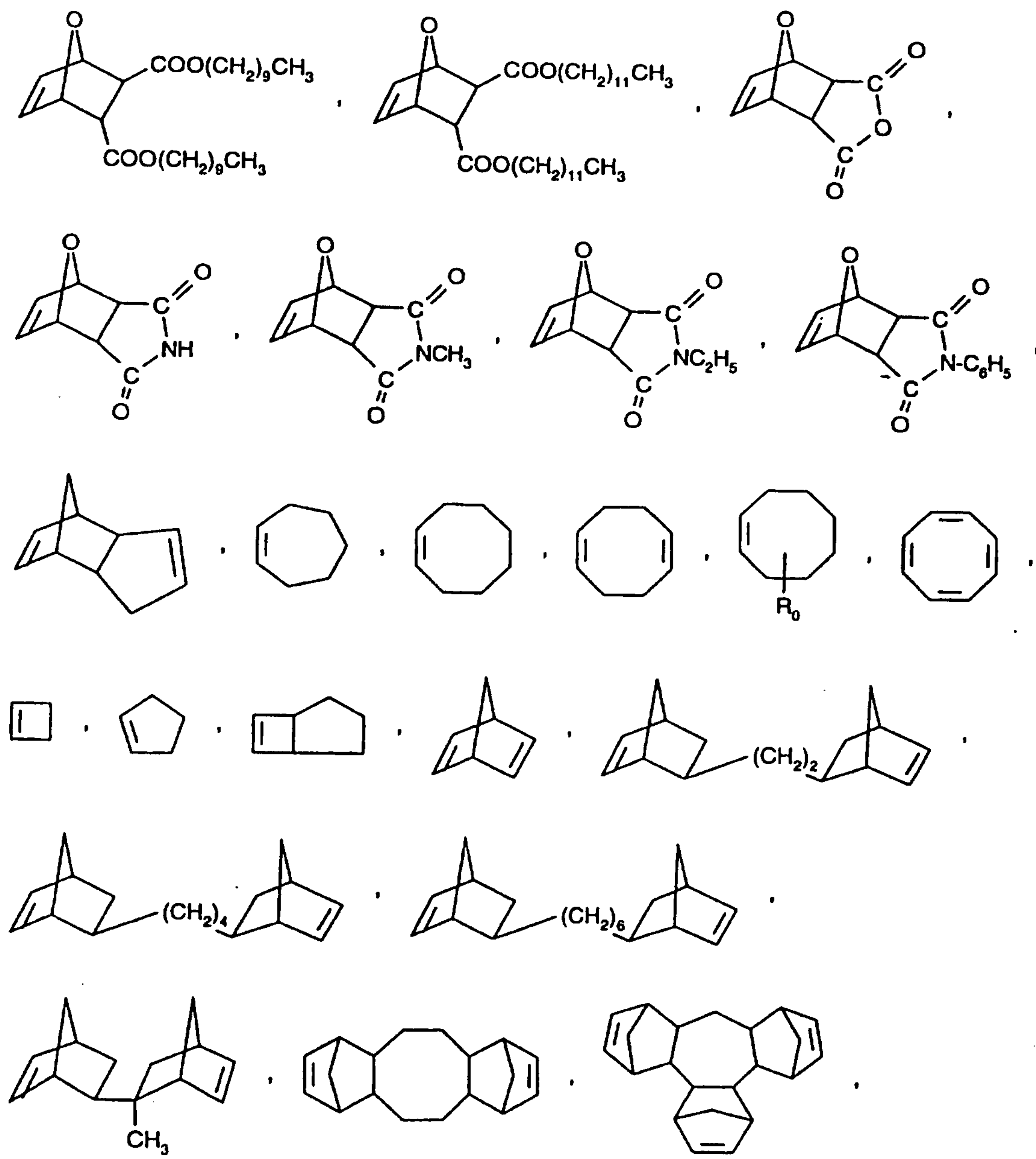
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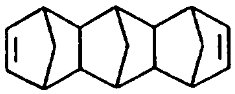
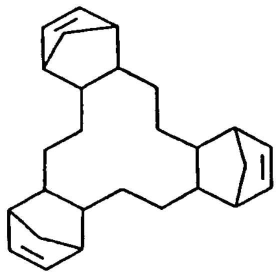
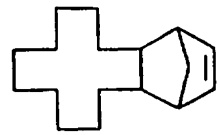
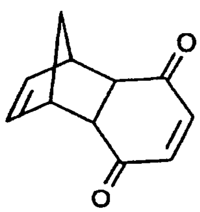
COO(CH2)9CH3
COO(CH2)11CH3
COO(CH2)11CH3
NH
NCH3
NC2H5
N-C6H5
R0
(CH2)2
(CH2)4
(CH2)6
CH3

 ,  ,  ,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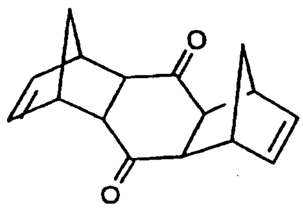
, 
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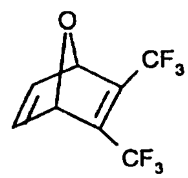
, 
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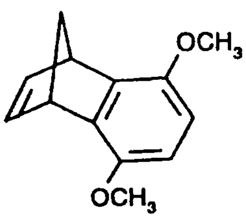
CF3
CF3
,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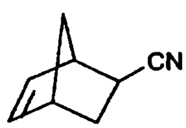
OCH3
, 
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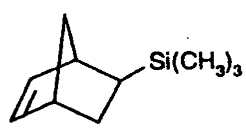
, 
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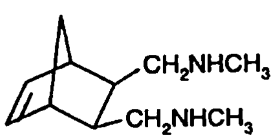
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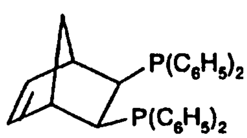
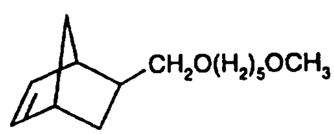
CH2NHCH3
, 
P(C6H5)2
P(C6H5)2
, 
CH2O(H2)5OCH3
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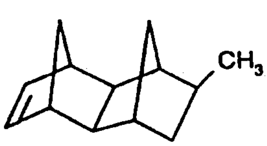
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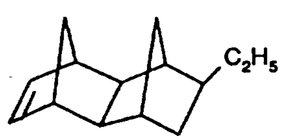
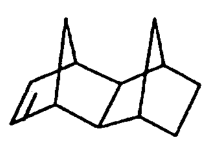
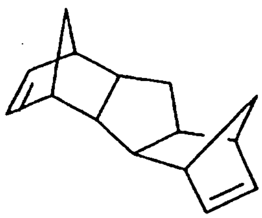
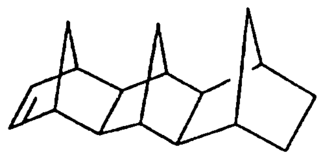
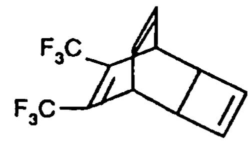
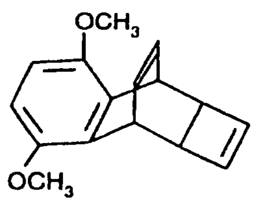
, 
C2H5
,  ,

 ,  ,  and

 .

R_0 can, for example, be an epoxy, acrylate or methacrylate group which is covalently bonded to the cyclooctene directly or *via* a bridge group.

Condensed and/or bridged and/or linked olefinically unsaturated ring systems are generally prepared by means of Diels-Alder reactions. Within the scope of the invention, "meltable without decomposition" means that strained cycloolefins can be melted and the catalyst can be dissolved. In the case of thermally labile strained cycloolefins it may therefore be necessary to dissolve the catalyst under pressure. Where the reaction temperature is higher than the decomposition temperature of the strained cycloolefin, it is advisable to carry out the procedures under pressure in order to avoid decomposition of the monomers prior to polymerisation.

In a preferred embodiment, the compositions according to the invention additionally contain an acetylene or a diene, preferably a 1,3-diene, for example in amounts of from 0.000001 to 5 % by weight, preferably from 0.000001 to 3 % by weight, based on the strained cycloolefin. Cyclic dienes are preferred. Some examples of open-chain and cyclic dienes are butadiene, norbornadiene, cyclopentadiene, cyclohexa-1,3-diene, cyclohepta-1,3-diene, cycloocta-1,3-diene and cycloocta-1,5-diene. Suitable acetylenes are mono- or di-substituted. Some examples are methylacetylene, ethylacetylene, n- or iso-propylacetylene, n-, iso- and tert-butylacetylene, trimethylsilylacetylene, dimethylacetylene, methyl-ethylacetylene and dipropylacetylene. Depending upon the acetylene or diene chosen, a

catalyst used according to the invention can be selectively partially inhibited and the processing time prolonged.

X_{01} and X_{02} in formulae I and Ia are preferably F, Cl or Br, especially Cl or Br, and are more especially each Cl.

Me in formulae I and Ia is preferably ruthenium.

In a preferred embodiment, T_3 is a hydrogen atom or T_3 is a hydrocarbon radical having from 1 to 16, preferably from 1 to 12, carbon atoms as defined within the scope of the invention.

T_3 as alkyl may contain preferably from 1 to 8 and especially from 1 to 6 carbon atoms. Some examples of alkyl are methyl, ethyl and the isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. T_3 is especially linear C_1-C_4alkyl.

T_3 as cycloalkyl may contain preferably from 5 to 8 carbon atoms. Cyclopentyl and cyclohexyl are especially preferred.

T_3 as heterocycloalkyl may preferably contain 4 or 5 carbon atoms and preferably a hetero atom selected from the group -O-, -S- and -N-. Some examples are tetrahydrofuranyl, pyrrolidinyl, piperazinyl and tetrahydrothiophenyl.

T_3 as aryl may contain preferably from 6 to 10 carbon atoms. Preferred examples are naphthyl and especially phenyl.

T_3 as heteroaryl may contain preferably 4 or 5 carbon atoms and one or two hetero atoms selected from the group -O-, -S- and -N-. Some examples are furanyl, thiophenyl, pyrrolyl, pyridinyl and pyrimidinyl.

Preferred substituents for T_3 are methyl, ethyl, methoxy, ethoxy, trichloromethyl, trifluoromethyl, phenyl, phenyloxy, F and Cl.

In a preferred embodiment, T_3 is hydrogen, C_1-C_4alkyl, cyclopentyl, cyclohexyl, phenyl or naphthyl, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl, phenyl, F or Cl.

In formula Ia, T_4 contains as arene preferably from 6 to 12 carbon atoms and as hetero-arene preferably from 4 to 11 carbon atoms and preferably from 1 to 3 hetero atoms from the group O, S and N. Some examples of substituents for T_4 are methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, methoxy, ethoxy, trifluoromethyl, F and Cl. Preferred arenes and heteroarenes are benzene, toluene, xylene, trimethylbenzene, naphthalene, biphenyl, anthracene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, fluoranthrene, furan, thiophene, pyrrole, pyridine, γ-pyran, γ-thiopyran, pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isooxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene and purine. Arenes and heteroarenes that are given greater preference are benzene, naphthalene, cumene, thiophene and benzothiophene. Special preference is given to the arene benzene or a C_1-C_4alkyl-substituted benzene, for example toluene, xylene, isopropylbenzene, tert-butylbenzene or cumene, and special preference is given to the heteroarene thiophene.

Phosphine groups T_1 and T_2 are preferably tertiary phosphines, or ditertiary diphosphines having from 3 to 40, preferably from 3 to 30 and especially from 3 to 24, carbon atoms.

The phosphine ligands preferably correspond to formulae VII and VIIa,

$$PR_{26}R_{27}R_{28} \qquad (VII),$$

$$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27} \qquad (VIIa),$$

wherein

R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_{20}alkyl; C_4-C_{12}cycloalkyl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by C_1-C_6alkoxy; C_6-C_{16}aryl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by

C_1-C_6alkoxy; or C_7-C_{16}aralkyl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6-haloalkyl, -NO_2 or by C_1-C_6alkoxy; or

the radicals R_{26} and R_{27} together form tetra- or penta-methylene that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, -NO_2 or by C_1-C_6alkoxy, or tetra- or penta-methylene that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, -NO_2 or by C_1-C_6alkoxy and condensed with one or two 1,2-phenylene groups, and

R_{28} is as defined above; and

Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene having from 4 to 8 carbon atoms; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene having 5 or 6 ring members and a hetero atom from the group O and N; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2-phenylene, 1-methylene-phen-2-yl; 1,2-dimethylenebenzene; or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 2,2'-biphenylene.

The radicals R_{26}, R_{27} and R_{28} are preferably identical radicals. Radicals R_{26}, R_{27} and R_{28} that are sterically demanding, for example cyclic or branched, especially α- and more especially α,α-di-branched alkyl groups, are especially preferred.

When R_{26}, R_{27} and R_{28} are substituted, the substituents are preferably C_1-C_4alkyl, C_1-C_4haloalkyl or C_1-C_4alkoxy. Halogen is preferably Cl and especially F. Examples of preferred substituents are methyl, methoxy, ethyl, ethoxy and trifluoromethyl. R_{26}, R_{27} and R_{28} may be substituted, for example, by from 1 to 3 substituents.

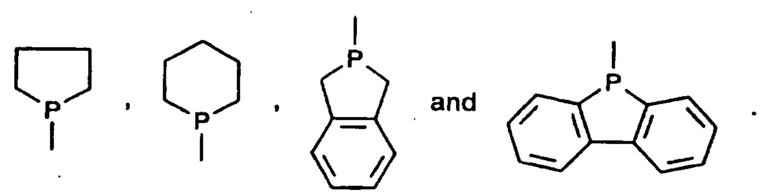
R_{26}, R_{27} and R_{28} as alkyl may be linear or branched and contain preferably from 1 to 12, especially from 1 to 8 and more especially from 1 to 6, carbon atoms. Examples of alkyl are methyl, ethyl, n- and iso-propyl, n-, iso- and tert-butyl, and the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl and eicosyl. Preferred examples are methyl, ethyl, n- and iso-propyl, n-, iso- and tert-butyl, 1-, 2- or 3-pentyl and 1-, 2-, 3- or 4-hexyl. Sterically demanding branched alkyl groups are especially preferred.

When R_{26}, R_{27} and R_{28} are cycloalkyl, they are preferably C_5-C_8cycloalkyl and especially C_5- or C_6-cycloalkyl. Some examples are cyclobutyl, cycloheptyl, cyclooctyl and especially cyclopentyl and cyclohexyl. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethyl-cyclopentyl and -cyclohexyl.

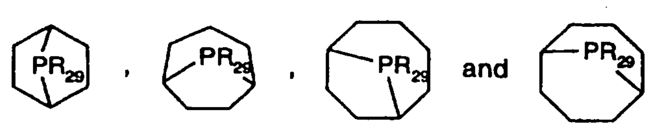
When R_{26}, R_{27} and R_{28} are aryl, they are preferably C_6-C_{12}aryl and especially phenyl or naphthyl. Examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethyl-phenyl.

When R_{26}, R_{27} and R_{28} are aralkyl, they are preferably C_7-C_{13}aralkyl, the alkylene group in the aralkyl preferably being methylene. Aralkyl is especially benzyl. Examples of substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethyl-benzyl.

Examples of unsubstituted or substituted and/or condensed tetra- and penta-methylene bonded to the P atom are:



Other suitable phosphines are cycloaliphates having from 6 to 8 ring carbon atoms and bridged by a $=PR_{29}$ group, for example



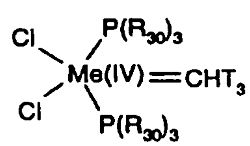
wherein R_{29} is C_1-C_6alkyl, cyclohexyl, benzyl, or phenyl that is unsubstituted or substituted by one or two C_1-C_4alkyl substituents.

Z_1 as linear or branched alkylene is preferably 1,2-alkylene or 1,3-alkylene having preferably from 2 to 6 carbon atoms, for example ethylene, 1,2-propylene or 1,2-butylene.

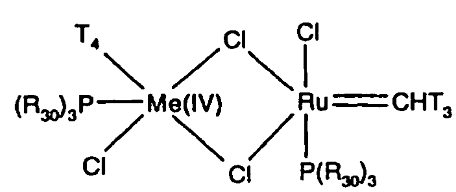
Examples of Z_1 as cycloalkylene are 1,2- and 1,3-cyclopentylene and 1,2- or 1,3-cyclohexylene. Examples of Z_1 as heterocycloalkylene are 1,2- and 1,3-pyrrolidine, 1,2- and 1,3-piperidine and 1,2- and 1,3-tetrahydrofuran.

In a preferred embodiment, the phosphine ligands correspond to formula VII wherein R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_6alkyl; unsubstituted or C_1-C_4-alkyl-substituted cyclopentyl or cyclohexyl; unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or trifluoromethyl-substituted phenyl; or unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or trifluoromethyl-substituted benzyl. Especially preferred examples of phosphine ligands of formula VII are $(C_6H_5)_3P$, $(C_6H_5CH_2)_3P$, $(C_5H_{11})_3P$, $(CH_3)_3P$, $(C_2H_5)_3P$, (n-$C_3H_7)_3P$, (iso-$C_3H_7)_3P$, (n-$C_4H_9)_3P$, (2-methyl-$C_6H_4)_3P$, (3-CH_3-$C_6H_4)_3P$, (4-CH_3-$C_6H_4)_3P$, (2,4-di-CH_3-$C_6H_3)_3P$, (2,6-di-CH_3-$C_6H_3)_3P$, (2-C_2H_5-$C_6H_4)_3P$, (3-C_2H_5-$C_6H_4)_3P$, (4-C_2H_5-$C_6H_4)_3P$, (2-n-C_3H_7-$C_6H_4)_3P$, (3-n-C_3H_7-$C_6H_4)_3P$, (4-n-C_3H_7-$C_6H_4)_3P$, (2-iso-C_3H_7-$C_6H_4)_3P$, (3-iso-C_3H_7-$C_6H_4)_3P$, (4-iso-C_3H_7-$C_6H_4)_3P$, (2-n-C_4H_9-$C_6H_4)_3P$, (3-n-C_4H_9-$C_6H_4)_3P$, (4-n-C_4H_9-$C_6H_4)_3P$, (2-iso-C_4H_9-$C_6H_4)_3P$, (3-iso-C_4H_9-$C_6H_4)_3P$, (4-iso-C_4H_9-$C_6H_4)_3P$, (2-tert-C_4H_9-$C_6H_4)_3P$, (3-tert-C_4H_9-$C_6H_4)_3P$, (4-tert-C_4H_9-$C_6H_4)_3P$, (2-CH_3-6-tert-C_4H_9-$C_6H_3)_3P$, (3-CH_3-6-tert-C_4H_9-$C_6H_3)_3P$, (3-CH_3-6-tert-C_4H_9-$C_6H_3)_3P$, (2,6-di-tert-C_4H_9-$C_6H_3)_3P$, (2,3-di-tert-C_4H_9-$C_6H_3)_3P$ and (2,4-di-tert-C_4H_9-$C_6H_3)_3P$.

A preferred subgroup of compounds of formulae I and Ia is formed by those of formulae Ib and Ic



(Ib),



(Ic),

wherein

Me is Ru or Os,

R_{30} is α-branched C_3-C_8alkyl; C_5-C_8cycloalkyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; or C_6-C_{10}aryl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$;

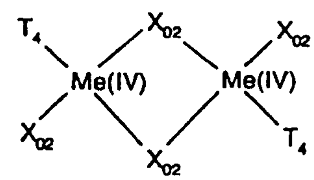
T_3 is hydrogen; C_1-C_8alkyl; C_5-C_8cycloalkyl that is unsubstituted or substituted by C_1-C_4-alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; or C_6-C_{10}aryl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; and

T_4 is phenyl, or phenyl substituted by from one to three C_1-C_4alkyl substituents.

Some specific and preferred examples are [Me is Os(IV) and preferably Ru(IV)]: $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}Cl)$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}Br)$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}NO_2)$, $Br_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}OC_2H_5)$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}CH_3)$, $F_2[P(C_5H_9)_3]_2Me{=}CH[C_6H_3{-}(CH_3)_2]$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_{10}H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_3$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CHCH_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}iso{-}C_3H_7$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}tert{-}C_4H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}n{-}C_4H_9$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_4{-}OCH_3$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_3{-}(CH_3)_2$, $Br_2[P(C_6{-}H_{11})_3]_2Me{=}CH{-}C_6H_2{-}(CH_3)_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_2C_6H_5$, $Cl_2[P(tert{-}C_4H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(iso{-}C_3H_7)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_5)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_4{-}H_3)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_4{-}(CH_3)_2)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_2{-}(CH_3)_3)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3{-}CH_2CH_2{-}P(C_6H_{11})_3]Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_{11}$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_5H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_{11}$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH_2$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH_2$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_4{-}CH(CH_3)_2$ and $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}n{-}C_4H_9$.

The compounds of formula I are known and the preparation thereof is described by Schwab et al. [Schwab, P., France, M.B., Ziller, J.W., Grubbs, R.H., Angew. Chem. 107:2179-2181 (1995)]. The dinuclear compounds of formula Ia can be prepared, for example, by reacting

two equivalents of a compound of formula I with one equivalent of a compound known *per se* of the formula



wherein X_{02}, Me and T_4 are as defined for formula Ia, in the presence of an inert solvent.

The composition according to the invention may additionally contain further open-chain comonomers that form copolymers with the strained cycloolefins. When dienes are additionally used, for example, cross-linked polymerisates may be formed. Some examples of such comonomers are olefinically mono- or di-unsaturated compounds, such as olefins and dienes from the group ethene, propene, butene, pentene, hexene, heptene, octene, decene, dodecylene, cyclohexene (which, as is known, does not form metathesis polymers on its own), acrylic and methacrylic acid and the esters and amides thereof, vinyl ethers, vinyl esters, vinyl chloride, vinylidene chloride, styrene, butadiene, isoprene and chlorobutadiene. When volatile comonomers are additionally used, it is often necessary to carry out the procedures under pressure. The additional use of non-volatile comonomers can therefore be of advantage to the method.

The further open-chain olefins suitable for copolymerisation are present in the composition according to the invention for example in an amount of up to 80 % by weight, preferably from 0.1 to 80 % by weight, especially from 0.5 to 60 % by weight and more especially from 5 to 40 % by weight, based on the total amount of compounds of formula II and further olefins capable of copolymerisation.

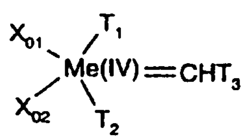
Within the scope of this invention, a catalytic amount is preferably an amount of from 0.001 to 20 mol %, especially from 0.01 to 15 mol %, more especially from 0.01 to 10 mol %, and very especially from 0.01 to 5 mol %, based on the amount of monomer. Because ruthenium and osmium catalysts containing phosphine groups have a high catalytic activity,

amounts of from 0.001 to 2 mol % are often sufficient, however, and are therefore especially preferred.

The composition according to the invention may contain formulation auxiliaries. Known auxiliaries are antistatics, antioxidants, light stabilisers, plasticisers, dyes, pigments, fillers, reinforcing fillers, lubricants, adhesion promoters, viscosity-increasing agents and demoulding auxiliaries. The fillers may be present in surprisingly high proportions without having an adverse effect on the polymerisation, for example in amounts of up to 80 % by weight, preferably from 1 to 70 % by weight, especially from 5 to 70 % by weight, more especially from 5 to 60 % by weight and very especially from 10 to 60 % by weight, based on the composition. A great variety of fillers and reinforcing fillers for improving the optical, physical, mechanical and electrical properties is known. Some examples are glass and quartz in the form of powders, beads and fibres, metal and semi-metal oxides, carbonates such as $MgCO_3$, $CaCO_3$, dolomite, metal sulfates such as gypsum and barite, natural and synthetic silicates such as talc, zeolites, wollastonite, feldspars, argillaceous earths, such as China clay, crushed stone, whiskers, carbon fibres, plastics fibres or powders, and carbon black. Viscosity-increasing agents are especially metathesis polymerisates that have olefinically unsaturated groups and can be incorporated into the polymer during polymerisation. Such metathesis polymerisates are known and are commercially available, for example, under the trade name Vestenamere®. For the same purpose it is also possible to use, for example, poly-1,3-dienes such as polybutadiene, polyisoprene, polychlorobutadiene or copolymers with the basic dienes and one or more olefins. Such polymers are also commercially available, for example Buna® and Kraton®. The amount of viscosity-increasing polymers can be, for example, from 0.1 to 50 % by weight, preferably from 1 to 30 % by weight and especially from 1 to 20 % by weight, based on all the monomers present in the composition. The viscosity-increasing agents serve simultaneously to improve the ductility characteristics of the polymers.

The compositions according to the invention are excellently suitable for the direct production of shaped articles. Despite the high catalyst activity, the individual components can be mixed and brought into the desired form because the catalysts very surprisingly dissolve in non-polar and polar monomers even at room temperature or with slight heating and therefore allow sufficient processing time.

The invention relates also to a method of preparing polymerisates by thermal metathesis polymerisation, which method comprises heating a solventless composition comprising
(a) at least one strained cycloolefin, and
(b) a catalytic amount of at least one compound of formula I or Ia



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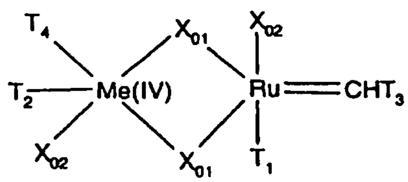


(Ia),

wherein

Me is ruthenium or osmium;

T_1 and T_2 are each independently of the other a tertiary phosphine or T_1 and T_2 together form a ditertiary diphosphine;

T_3 is hydrogen, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group -O-, -S- and -N-, C_6-C_{14}aryl or C_4-C_{15}heteroaryl having from one to three hetero atoms selected from the group -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or by halogen;

T_4 is C_6-C_{18}arene or C_4-C_{15}heteroarene each of which is unsubstituted or substituted by from one to three C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br substituents, and

X_{01} and X_{02} are each independently of the other halogen.

The preferences already indicated in respect of the composition apply also to the method according to the invention.

The compositions according to the invention are not stable in storage and monomers and catalyst should be mixed together only just before processing. The method according to the invention is advantageously carried out in such a manner that shaping, for example to give a coating or a moulding, is combined with the mixing and takes place prior to the polymerisation. In principle, all known shaping procedures, for example extrusion, injection moulding and compression procedures, can be used. The compositions according to the invention are suitable especially as casting resins where appropriate with the application of pressure, for example as in RIM-processes (Reaction Injection Moulding).

"Heating" may represent a temperature from room temperature up to 300°C, preferably from 30 to 300°C, especially from 40 to 250°C, more especially from 50 to 200°C, and very especially from 60 to 180°C. The polymerisation times depend essentially upon the catalyst activity and the times vary from seconds through minutes up to several hours. The polymerisation can also be carried out stepwise with increasing temperatures.

Using the method according to the invention it is possible to produce materials (semi-finished articles) for the production of mouldings by means of machining techniques or to produce directly all kinds of mouldings, films, foils and coatings. The invention relates also to the use of the composition according to the invention for the production of semi-finished articles, mouldings and foils. The invention relates also to mouldings made from the compositions according to the invention.

Depending upon the monomer used, the polymers according to the invention may have very different properties. Some are distinguished by a very high degree of oxygen permeability, low dielectric constants, good thermal stability and low water absorption. Others have excellent optical properties, for example high transparency and low refractive indices. Special mention should also be made of the low degree of shrinkage. They can therefore be used in a very wide variety of technical fields. The avoidance of solvents ensures the production of bubble-free mouldings and coatings even at relatively high polymerisation temperatures.

When used as coatings on the surfaces of support materials, especially non-polar support materials, the compositions according to the invention are distinguished by high adhesive

strength. A physical treatment (for example plasma treatment) or chemical treatment (application of adhesion promoters) can further improve the adhesive strength. The coated materials are also distinguished by a very high degree of surface smoothness and gloss. Among their good mechanical properties, special mention should be made of the low degree of shrinkage and the high impact strength, and also the thermal stability. In addition, they can be readily demoulded when processed in moulds and have a high resistance to solvents. The properties desired in final use can be adjusted selectively by way of the monomers chosen. In addition to rigid and resilient thermoplastic mouldings it is also possible to obtain cross-linked thermosetting or elastomeric polymerisates.

Those polymers are suitable for the production of medical apparatus, implants or contact lenses; for the production of electronic components; as binders for surface-coatings; as photocurable compositions for model-making or as adhesives for bonding substrates having low surface energies (for example Teflon, polyethylene and polypropylene).

The compositions according to the invention are especially suitable for the production of protective coatings on substrates or support materials and relief images. The invention relates also to a variant of the method according to the invention for the preparation of coatings on support materials in which a composition according to the invention is applied as a coating to a support, for example by means of immersion, spreading, pouring, rolling, knife-application or centrifugal casting procedures, and the coating is heated for the purpose of polymerisation. This may be followed by heat treatment. Surfaces of substrates can be modified or protected using that method.

The present invention relates also to a coated material comprising (a) a support material and (b) a coating of a composition according to the invention which is applied to at least one surface.

The present invention relates likewise to a coated material comprising (a) a support material and (b) a polymeric coating of a composition according to the invention which is applied to at least one surface.

Suitable substrates (support materials) are, for example, glass, minerals, ceramics, plastics, wood, semi-metals, metals, metal oxides and metal nitrides. The coating thicknesses

depend essentially upon the desired use and may be, for example, from 0.1 to 1000 μm, preferably from 0.5 to 500 μm, especially from 1 to 100 μm. The coated materials are distinguished by high adhesive strength and good thermal and mechanical properties.

The production of the coated materials according to the invention can be carried out in accordance with known methods, for example spreading, knife-application or pouring processes, such as curtain coating or centrifugal casting.

The compositions according to the invention are suitable also for the preparation of rubber-like or thermoplastic polymerisates which can be further cross-linked. For that purpose the strained cycloolefins may contain reactive groups, for example (meth)acrylate or epoxy groups, which are covalently bonded to the cycloolefin directly or *via* a bridge group.

The compositions according to the invention can also be used as thermally curable adhesives for firm bonding to an extremely wide variety of materials, it being possible to achieve excellent peel resistance.

In addition to having high adhesive strengths, excellent processability, good surface properties (smoothness, gloss), high cross-linking density and resistance to solvents and other liquids, the polymerisates according to the invention are also distinguished especially by very good physico-mechanical properties, for example high thermal stability, breaking and flexural strength and impact strength, and excellent electrical properties, for example low conductivities, dielectric constants and (ε)- and ($\tan \delta$)-loss factors. In addition, mention should be made of the high oxygen permeability and low water absorption. Polymers composed only of carbon and hydrogen are especially valuable from the ecological stand-point because they can, for example, be completely recycled by pyrolysis or harmlessly burned.

The following Examples illustrate the invention in more detail.

The following catalysts are used:
$Cl_2[P(C_5H_9)_3]_2Ru(IV)=CH\text{-}C_6H_5$ (catalyst A).
$Cl_2[P(C_6H_{11})_3]_2Ru(IV)=CH\text{-}C_6H_5$ (catalyst B).

$Cl_2[P(C_6H_{11})_3]_2Ru(IV)=CH-C_6H_4-CH(CH_3)_2$ (catalyst C).

Examples B1 to B13:

The catalyst is dissolved in the monomer, powdered quartz (if used) is added and the mixture is homogenised by stirring. The mixture is then degassed *in vacuo*. The mixture is poured into moulds and heated. Further data are given in Table 1.

The glass transition temperature is determined by means of differential thermal analysis (heating rate 10°C/min). Swelling is determined by soaking in toluene (the percentage increase in weight after 24 hours' storage in toluene is a measure of the cross-linking density). The percentage weight loss is determined by thermogravimetry at a heating rate of 10°C/min up to 300°C.

Table 1:

Example No.	Catalyst (% by wt.)	Monomer	Curing cycle (h/°C)	T_g (°C)	Weight loss (%)	Swelling (%)	Remarks
B1	B (0.1)	DCPD[1]	2/120	76	20.4	75	after about 1 min. rubber-like, then solid
B2	A(0.5)	DCPD[1]	2/120	159	1.0	83	after 30 to 45 sec at 35°C solid
B3	B(0.1)	DCPD[2]	[6]	10	29	94	rubber
B4	A(0.1)	DCPD[2]	[6]	14	31	79	rubber
B5	B(0.3)	DCPD[2]	[6]	150	1.0	64	solid panel
B6	A(0.3)	DCPD[2]	[6]	108	1.1	72	solid panel
B7	A(0.3[3])	DCPD[2]/60 % by weight quartz W12	[6]	123	--	--	solid panel
B8	B(0.3)	norbornene-carboxylic acid methyl	1/120	73	0.8	>400	solid panel

Example No.	Catalyst (% by wt.)	Monomer	Curing cycle (h/°C)	T_g (°C)	Weight loss (%)	Swelling (%)	Remarks
		ester					
B9	C(0.2)	DCPD[4]	[7]	129	2.3		almost colourless panel
B10	C(0.1)	DCPD[4]	[7]	115	3.0		almost colourless panel
B11	C(0.2)	DCPD[5]	[7]	144	2.5		almost colourless panel
B12	C(0.1)	DCPD[5]	[7]	126	3.5		almost colourless panel
B13	C(0.05)	DCPD[5]	[7]	<R.T			rubber

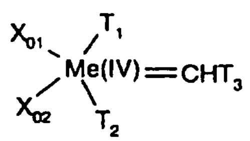
DCPD: dicyclopentadiene; [1]: distilled and purified; [2]: technical; [3]:based on DCPD;
[4]: DCPD Shell degassed (approx. 97% purity); [5]: DCPD BF Goodrich pure (>98.0% purity);
[6]: 1/100; 1/120; 4/150; [7]: 1/80; 1/100; 2/120
B9 to B12: Increase in viscosity immediately after the addition of the catalyst.

Example B14:
DCPD (technical) is homogenised with 0.1 % by weight catalyst A and left to stand at room temperature. The mixture is viscous only after 24 hours and after 4 days it is solid and rubber-like.

Example B15:
DCPD (technical) is homogenised with 0.1 % by weight catalyst B and left to stand at room temperature. The mixture is semi-solid only after 24 hours and after 4 days it is solid and rubber-like.
Examples B14 and B15 show that the technical DCPD is completely polymerised using these catalysts; the polymerisation is considerably slower than when purified (freshly distilled) DCPD is used.

What is claimed is:

1. A solventless polymerisable composition comprising
(a) at least one strained cycloolefin that is liquid or is meltable without decomposition, and
(b) a catalytic amount of at least one compound of formula I or Ia or a mixture of compounds of formulae I and Ia



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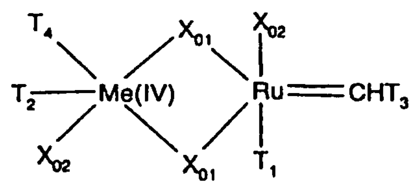


(Ia),

wherein

Me is ruthenium or osmium;

T_1 and T_2 are each independently of the other a tertiary phosphine or T_1 and T_2 together form a ditertiary diphosphine;

T_3 is hydrogen, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having from one to three hetero atoms selected from the group -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or by halogen;

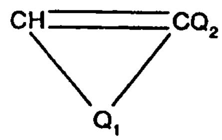
T_4 is C_6-C_{18}arene or C_4-C_{15}heteroarene each of which is unsubstituted or substituted by from one to three C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br substituents, and

X_{01} and X_{02} are each independently of the other halogen.

2. A composition according to claim 1, wherein the cyclic olefin is a monocyclic or polycyclic condensed and/or bridged and/or linked ring system which is unsubstituted or substituted,

which contains hetero atoms in one or more rings or contains no hetero atoms, and which contains condensed aromatic or heteroaromatic rings or contains no such rings.

3. A composition according to claim 1, wherein the cycloolefin corresponds to formula II



(II),

wherein

Q_1 is a radical having at least one carbon atom which, together with the -CH=CQ_2- group, forms an at least 3-membered alicyclic ring which may contain one or more hetero atoms selected from the group Si, P, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, -NO_2, $R_1R_2R_3$Si-$(O)_u$-, -COOM, -SO_3M, -PO_3M, -COO$(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}hydroxyalkyl, C_1-C_{20}haloalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms, when present, are substituted by -CO-O-CO- or by -CO-NR_5-CO-; or wherein an alicyclic, aromatic or heteroaromatic ring has been fused to adjacent carbon atoms of the alicyclic ring, the former ring being unsubstituted or substituted by halogen, -CN, -NO_2, $R_6R_7R_8$Si-$(O)_u$-, -COOM, -SO_3M, -PO_3M, -COO$(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO-, -SO_2-, -O-C(O)-, -C(O)-O-, -C(O)-NR_5-, -NR_{10}-C(O)-, -SO_2-O- or -O-SO_2-; R_1, R_2 and R_3 are each independently of the others C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; R_4 and R_{13} are each independently of the other C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_{12}alkoxy or by C_3-C_8cycloalkyl; R_6, R_7 and R_8 are each independently of the others C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; and u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{12}alkoxy, halogen, -CN or R_{11}-X_2- wherein R_{11} is C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl and X_2 is -C(O)-O- or -C(O)-NR_{12}- wherein R_{12} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

the above-mentioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, $-NO_2$, -CN or by halogen, and the hetero atoms of the afore-mentioned heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group -O-, -S-, -NR_9- and -N=; and R_9 is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl.

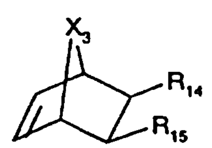
4. A composition according to claim 3, wherein Q_2 in formula II is hydrogen.

5. A composition according to claim 3, wherein the alicyclic ring formed in formula II by Q_1 together with the -CH=CQ_2- group has from 3 to 16 ring atoms.

6. A composition according to claim 3, wherein the alicyclic ring is a monocyclic, bicyclic, tricyclic or tetracyclic ring system.

7. A composition according to claim 1 which comprises as strained cycloolefin norbornene and norbornene derivatives, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene or cyclododecene.

8. A composition according to claim 7, wherein the norbornene derivatives correspond to formula III



(III),

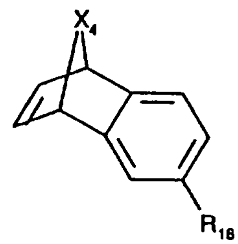
wherein

X_3 is -CHR_{16}-, oxygen or sulfur;

R_{14} and R_{15} are each independently of the other hydrogen, -CN, trifluoromethyl, $(CH_3)_3$Si-O-, $(CH_3)_3$Si- or -$COOR_{17}$; and

R_{16} and R_{17} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula IV



(IV),

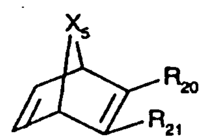
wherein

X_4 is $-CHR_{19}-$, oxygen or sulfur;

R_{18} is hydrogen, C_1-C_6alkyl or halogen; and

R_{19} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula V



(V),

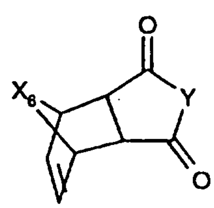
wherein

X_5 is $-CHR_{22}-$, oxygen or sulfur;

R_{20} and R_{21} are each independently of the other hydrogen, CN, trifluoromethyl, $(CH_3)_3Si$-O-, $(CH_3)_3Si$- or $-COOR_{23}$; and

R_{22} and R_{23} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula VI



(VI),

wherein

X_6 is $-CHR_{24}-$, oxygen or sulfur;

Y is oxygen or $>N-R_{25}$,

R_{24} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; and

R_{25} is hydrogen, methyl, ethyl or phenyl.

9. A composition according to claim 1, wherein the strained cycloolefin is dicyclopentadiene, oligocyclopentadienes and Diels-Alder adducts of cyclopentadiene with cycloolefins, cyclodienes or open-chain dienes.

10. A composition according to claim 1, wherein the cycloolefin is a monomer composed only of carbon and hydrogen.

11. A composition according to claim 1, wherein X_{01} and X_{02} in formulae I and Ia are F, Cl or Br.

12. A composition according to claim 11, wherein X_{01} and X_{02} are each Cl.

13. A composition according to claim 1, wherein Me in formulae I and Ia is Ru.

14. A composition according to claim 1, wherein T_3 is a hydrocarbon radical having from 1 to 16 carbon atoms or hydrogen.

15. A composition according to claim 1, wherein T_3 is hydrogen, C_1-C_4alkyl, cyclopentyl, cyclohexyl, phenyl or naphthyl, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4-alkoxy, C_1-C_4haloalkyl, phenyl, F or Cl.

16. A composition according to claim 1, wherein T_4 as arene is benzene or C_1-C_4alkyl-substituted benzene.

17. A composition according to claim 1, wherein the phosphine groups T_1 and T_2 are tertiary phosphines or ditertiary diphosphines having from 3 to 40 carbon atoms.

18. A composition according to claim 17, wherein the phosphine ligands correspond to formulae VII and VIIa

$$PR_{26}R_{27}R_{28} \qquad (VII),$$

$$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27} \qquad \text{(VIIa)},$$

wherein

R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_{20}alkyl; C_4-C_{12}cycloalkyl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by C_1-C_6alkoxy; C_6-C_{16}aryl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by C_1-C_6alkoxy; or C_7-C_{16}aralkyl that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6-haloalkyl, $-NO_2$ or by C_1-C_6alkoxy; or

the radicals R_{26} and R_{27} together form tetra- or penta-methylene that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by C_1-C_6alkoxy, or tetra- or penta-methylene that is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl, $-NO_2$ or by C_1-C_6alkoxy and condensed with one or two 1,2-phenylene groups, and

R_{28} is as defined above; and

Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene having from 4 to 8 carbon atoms; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene having 5 or 6 ring members and a hetero atom from the group O and N; unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2-phenylene, 1-methylene-phen-2-yl or 1,2-dimethylenebenzene; or unsubstituted or C_1-C_4alkyl- or C_1.C_4alkoxy-substituted 2,2'-biphenylene.

19. A composition according to claim 18, wherein the radicals R_{26}, R_{27} and R_{28} are identical.

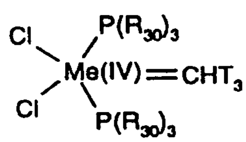
20. A composition according to claim 18, wherein Z_1 as linear or branched alkylene is a 1,2-alkylene or 1,3-alkylene having from 2 to 6 carbon atoms.

21. A composition according to claim 18, wherein the phosphine ligands correspond to formula VII wherein R_{26}, R_{27} and R_{28} are each independently of the others C_1-C_6alkyl; unsubstituted or C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl; unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or trifluoromethyl-substituted phenyl; or unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or trifluoromethyl-substituted benzyl.

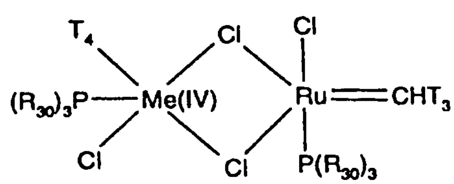
22. A composition according to claim 18, wherein the phosphine ligands of formula VII are $(C_6H_5)_3P$, $(C_6H_5CH_2)_3P$, $(C_5H_{11})_3P$, $(CH_3)_3P$, $(C_2H_5)_3P$, $(n\text{-}C_3H_7)_3P$, $(iso\text{-}C_3H_7)_3P$, $(n\text{-}C_4H_9)_3P$,

$(2\text{-methyl-}C_6H_4)_3P$, $(3\text{-}CH_3\text{-}C_6H_4)_3P$, $(4\text{-}CH_3\text{-}C_6H_4)_3P$, $(2,4\text{-di-}CH_3\text{-}C_6H_3)_3P$, $(2,6\text{-di-}CH_3\text{-}C_6H_3)_3P$, $(2\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(3\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(4\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(2\text{-n-}C_3H_7\text{-}C_6H_4)_3P$, $(3\text{-n-}C_3H_7\text{-}C_6H_4)_3P$, $(4\text{-n-}C_3H_7\text{-}C_6H_4)_3P$, $(2\text{-iso-}C_3H_7\text{-}C_6H_4)_3P$, $(3\text{-iso-}C_3H_7\text{-}C_6H_4)_3P$, $(4\text{-iso-}C_3H_7\text{-}C_6H_4)_3P$, $(2\text{-n-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-n-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-n-}C_4H_9\text{-}C_6H_4)_3P$, $(2\text{-iso-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-iso-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-iso-}C_4H_9\text{-}C_6H_4)_3P$, $(2\text{-tert-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-tert-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-tert-}C_4H_9\text{-}C_6H_4)_3P$, $(2\text{-}CH_3\text{-6-tert-}C_4H_9\text{-}C_6H_3)_3P$, $(3\text{-}CH_3\text{-6-tert-}C_4H_9\text{-}C_6H_3)_3P$, $(3\text{-}CH_3\text{-6-tert-}C_4H_9\text{-}C_6H_3)_3P$, $(2,6\text{-di-tert-}C_4H_9\text{-}C_6H_3)_3P$, $(2,3\text{-di-tert-}C_4H_9\text{-}C_6H_3)_3P$ and $(2,4\text{-di-tert-}C_4H_9\text{-}C_6H_3)_3P$.

23. A composition according to claim 1, wherein the compounds of formulae I and Ia correspond to a subgroup of formulae Ib and Ic



(Ib),



(Ic),

wherein

Me is Ru or Os,

R_{30} is α-branched C_3-C_8alkyl; C_5-C_8cycloalkyl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; or C_6-C_{10}aryl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$;

T_3 is hydrogen; C_1-C_8alkyl; C_5-C_8cycloalkyl that is unsubstituted or substituted by C_1-C_4-alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; or C_6-C_{10}aryl that is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or by $-NO_2$; and

T_4 is phenyl, or phenyl substituted by from one to three C_1-C_4alkyl substituents.

24. A composition according to claim 1, wherein the compounds of formula I are selected from the group
$Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}Cl)$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}Br)$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}NO_2)$, $Br_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}OC_2H_5)$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}CH_3)$, $F_2[P(C_5H_9)_3]_2Me{=}CH[C_6H_3{-}(CH_3)_2]$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_{10}H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_3$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CHCH_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}iso{-}C_3H_7$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}tert{-}C_4H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}n{-}C_4H_9$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_4{-}OCH_3$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_3{-}(CH_3)_2$, $Br_2[P(C_6{-}H_{11})_3]_2Me{=}CH{-}C_6H_2{-}(CH_3)_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_2C_6H_5$, $Cl_2[P(tert{-}C_4H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(iso{-}C_3H_7)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_5)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_4{-}CH_3)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_4{-}(CH_3)_2)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_2{-}(CH_3)_3)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3{-}CH_2CH_2{-}P(C_6H_{11})_3]Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_{11}$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_5H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_{11}$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH_2$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH_2$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_4{-}CH(CH_3)_2$ and $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}n{-}C_4H_9$, wherein Me is Os(IV) or Ru(IV).

25. A composition according to claim 1, wherein the compounds of formulae I and Ia are present in an amount of from 0.001 to 20 mol %, based on the amount of monomer.

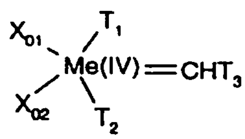
26. A composition according to claim 25, wherein the amount is from 0.001 to 2 mol %.

27. A composition according to claim 1 which additionally contains fillers.

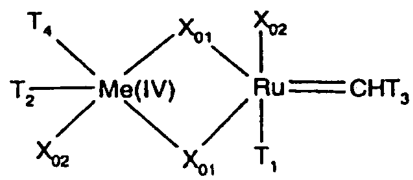
28. A composition according to claim 27, wherein the filler is present in an amount of up to 70 % by weight, based on the composition.

29. A method of preparing polymerisates by thermal metathesis polymerisation, which method comprises heating a solventless composition comprising
(a) at least one strained cycloolefin, and

(b) a catalytic amount of at least one compound of formula I od Ia



(I),



(Ia),

wherein

Me is ruthenium or osmium;

T_1 and T_2 are each independently of the other a tertiary phosphine or T_1 and T_2 together form a ditertiary diphosphine;

T_3 is hydrogen, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having from one to three hetero atoms selected from the group -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or by halogen;

T_4 is C_6-C_{18}arene or C_4-C_{15}heteroarene each of which is unsubstituted or substituted by from one to three C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br substituents, and

X_{01} and X_{02} are each independently of the other halogen.

30. A coated material comprising (a) a support material and (b) a coating of a composition according to claim 1 which is applied to at least one surface.

31. A coated material comprising (a) a support material and (b) a polymeric coating of a composition according to claim 1 which is applied to at least one surface.

32. A moulding formed of a composition according to claim 1.

33. The use of a composition according to claim 1 for the production of semi-finished articles, mouldings and foils.

INTERNATIONAL SEARCH REPORT

Intv onal Application No
PCI/EP 96/04375

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 04289 A (CALIFORNIA INST OF TECHN) 15 February 1996 see claims 1-25; example 12 -----	1-33

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 January 1997	24.01.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Stienon, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte nal Application No
PCT/EP 96/04375

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9604289	15-02-96	AU-A- 3272895	04-03-96